


Article

Mechanism of Ion-Diffusion Solid-Phase Reduction of Iron Oxides of Technogenic Origin in the Presence of the Liquid Phase and without it

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Abstract: The processes of iron oxides' reduction have a complex physicochemical mechanism, with the participation of solid, liquid, and gaseous substances. The article discusses the existing models for the reduction of iron oxides and provides data on the thermodynamic possibility of carrying out the reactions of their reduction through the solid and gas phases. Experimental data on the reduction of iron from industrial scale, obtained by the DSC (differential scanning calorimetry) method, show the kinetic dependence of the rate and completeness of recovery on external factors: pressing pressure during sample preparation and the reagents' composition. The pressing pressure, under conditions of iron ions' solid-phase diffusion, has the significant effect by increasing the reagents' contact area. Under conditions of iron ions' comprehensive diffusion, the pressing pressure does not affect the reduction processes rate. The introduction of 10 mass.% flux into the raw mixture composition leads to a partially liquid-phase diffusion of iron ions and weakens the effect of the pressing pressure in this process. An ion diffusion-catalytic mechanism is proposed to describe the observed effects during the reduction of iron oxide of technogenic origin.

Keywords: technogenic origin; iron oxides; thermodynamics; recovery; diffusion; metallization

1. Introduction

The long-term development of extractive industries in conditions of extensive nature management has led to the accumulation of a huge number of metallurgical, chemical, energy, and other technogenic formations. By now, in the locations of the largest and oldest metallurgical complexes, mineral reserves are being depleted. At the same time, accumulated technogenic formations can be a promising source of raw materials, of which iron is the most valuable for ferrous metallurgy. However, the accumulated technogenic formations at the same time are the source of environmental pollution. Involvement of technogenic formations in processing will help to solve the issues of limited resource base and environmental pollution [1–3]. Technogenic formation of the iron oxide is presented mostly by sludge and scale [3–5]. In such technogenic formations all iron oxides can be found simultaneously, and they are arranged in layers in the scale. The layered structure of the scale is completely consistent with the diagram of the iron-oxygen state. Above the temperature of 650 °C, the inner layer of scale consists of wustite (FeO), the middle layer of magnetite (Fe₃O₄), and the outer layer of hematite (Fe₂O₃) [6]. The properties of iron oxides according to [7] are presented in Table 1.

Table 1. Properties of Iron Oxides, data from [7].

Index	FeO	Fe ₂ O ₃		Fe ₃ O ₄
		α	γ	
Color	black	From dark-red to dark-purple	brown	black
Syngony	cubic	rhombohedral	cubic	cubic
Lattice parameter, Å	4.29	5.42 $\alpha = 55^\circ 17'$	8.34	8.38
Number of formula units in a cell	4	2	-	8
Space group	Fm3m	R3c	Fd3m	Fd3m
Melting point, °C	1370	1565	-	1600

Wustite (FeO) is a thermodynamically unstable compound. Below the temperature of 560 °C, it decays into α -Fe and magnetite (Fe₃O₄). The crystal lattice is cubic, $a = 4.29$ Å. The wustite crystal lattice always contains an excess of oxygen, so its composition corresponds more precisely to the nonstoichiometric formula FeO_{1.09}. As a result, the wustite crystal lattice contains a significant number of nonstoichiometry defects in the form of Fe²⁺ ion vacancies [8]. From a structural point of view, wustite refers to subtraction solid solutions: In its lattice, oxygen atoms occupy all the nodes in the anionic sublattice and some nodes in the cationic sublattice are not occupied by iron ions. If there is a lack of Fe²⁺ cations in the lattice, its electroneutrality is maintained due to the conversion of part of Fe²⁺ cations to Fe³⁺. So, this nonstoichiometric compound can be considered as a substitution solid solution of Fe₂O₃ in FeO [8].

Iron oxide α -Fe₂O₃ (hematite) is characterized by a rhombohedral corundum-type lattice with parameters $a = 5.42$ Å and $\alpha = 55^\circ 17'$. The unit cell of hematite is formed by four Fe³⁺ and six O²⁻ ions, which form a dense hexagonal package. One-third of the octahedral voids are vacant and two-thirds of them are filled with Fe³⁺ ions [6].

Magnetite (Fe₃O₄) has a cubic lattice of “reversed” spinel with $a = 8.38$ Å. Eight ions of Fe²⁺, 16 of Fe³⁺, and 32 of O²⁻ are present in the unit cell of magnetite. Oxygen ions form a dense cubic lattice containing 32 octahedral and 64 tetrahedral voids in a single unit cell. In this case eight ions of Fe²⁺ and the same amount of Fe³⁺ are distributed (statistically) in octahedral and the remaining eight Fe³⁺ in tetrahedral internodes. The presence of multivalent ions Fe²⁺ and Fe³⁺ in the same crystallographic positions (octahedral) facilitates the exchange of electrons and increase magnetite electrical conductivity [7].

Reduction of iron oxides in the physical and chemical aspects is considered to be heterogeneous processes, involving liquid, solid, and gaseous substances. The internal energy of the system continuously changes under the influence of both external (temperature) and internal (vapor pressure, reducing agent composition, degree of phase contact, etc.) parameters. The most important reducing agent of iron, widely used in metallurgical practice, is carbon. Several models have been proposed to describe the mechanism of metal oxides’ reduction by carbon [9–13]. S.I. Popel and his colleagues proposed four recovery schemes [14]. The first scheme is based on the most frequently used two-stage recovery scheme based on the adsorption-catalytic mechanism of G.I. Chufarov [15].

According to the first scheme, it is assumed that the process is carried out as a result of two simultaneous reactions:



The reduction of iron oxide in this scheme occurs through CO, and the role of solid carbon is reduced to the regeneration of carbon oxide by the Boudoir reaction.

According to the second (dissociative) scheme, the reduction of metals with a sufficiently high dissociation elasticity ($-\Delta P_{O_2}^0 \geq 1$ Pa) can proceed by dissociation of the oxide and subsequent interaction of molecular oxygen with carbon:



According to the third scheme, if the reduction and sublimation temperatures of the oxide are close, the interaction of the oxide and the reducing agent is possible due to the evaporation of the oxide with subsequent condensation (adsorption) of its vapors on the carbon surface, where the reduction process occurs:



In this way, it is possible to reduce the volatile oxides of MoO_3 , WO_3 , Nb_2O_3 , etc.

According to the fourth scheme, the reduction occurs directly during contact of solid phases: the interaction of solid carbon and oxide. This is one of the limiting factors in the scheme implementation. At the beginning, this contact is direct. After formation of separating layer of metal or lower oxide, it is carried out by the diffusion of reagents through this layer. According to the authors [11], the flow of the fourth scheme is very possible, but its contribution to the overall kinetics of metals' direct reduction from oxides is negligible, since the actual particles' contact surface is an insignificant fraction of their total surface. The second limiting factor of the fourth scheme possibility is the diffusion of reagents, which is quite slow at low temperatures.

According to [16], all the described schemes are based on outdated provisions of the atomic-molecular theory of reduction, which represents atoms as solid indivisible balls, and does not take into account advances in the study of the fine structure of matter and physical theories describing the behavior of elementary particles that make up atoms.

Thermodynamic Analysis of the Reactions of Iron Oxides' Reduction

The total reaction of all four schemes is the Reaction (9):



In relation to a specific iron oxide, this interaction is possible by the following Reactions (10)–(12):



Reduction of specific iron oxides through the gas phase is possible by Reactions (13)–(15):



According to [17], when cementite is formed in the system by Reaction (16):



it is also possible to reduce iron through the gas phase by Reaction (17):



Thermodynamic calculations were performed to determine the temperature range in which the reduction reactions of specific iron oxides can occur through the solid and gas phases. The results of calculating the Gibbs free energy for Reactions (11)–(18) are shown in Table 2.

Table 2. Value of Gibbs Free Energy of Iron Oxide Reduction Reactions.

Reaction №	ΔG^0_T , J/mol, at Temperature, °C					
	500	600	700	800	900	1000
10	151.2	47.3	−55.6	−158.0	−260.4	−362.5
11	136.9	71.1	6.0	−58.9	−123.9	−188.8
12	33.7	18.3	2.9	−12.5	−27.9	−43.3
13	−30.3	−29.2	−27.7	−26.5	−25.4	−24.5
14	−1.0	0.2	1.4	2.6	3.8	4.8
15	−1.6	0.7	2.9	5.0	7.0	8.9
16	26.3	15.6	5.0	−5.4	−15.7	−25.8
17	6.8	3.2	−0.4	−4.1	−7.9	−11.9

According to the data presented in Table 2, reduction of Fe_2O_3 oxide (Reaction (10)) by direct interaction of solid phases is thermodynamically possible starting from the temperature of 700 °C, and Fe_3O_4 and FeO (Reactions (11) and (12)) starting from the temperature of 800 °C. Through the gas phase, reduction of Fe_2O_3 (Reaction (13)) is possible in the entire temperature range (from room temperature to 1000 °C). Above the temperature of 600 °C, recovery through the gas phase of Fe_3O_4 and FeO (Reactions (14) and (15)) is thermodynamically impossible. Since, in accordance with the principle of sequence of transformations formulated by A.A. Baikov [18], above the temperature of 570 °C, the transition from higher iron oxides to lower ones proceeds according to the scheme:



According to the data [18] given in Table 3, the content of Fe_2O_3 in the scale at a temperature above 700 °C is insignificant, so it is very likely that above this temperature the reduction of Fe_3O_4 and FeO occurs only with the participation of solid carbon in the Reactions (11) and (12). Above the temperature of 700 °C through the gas phase, it is also possible to restore iron by Reaction (17), but this will only happen if cementite is formed in the system by Reaction (16).

Since above the temperature of 700 °C for Fe_2O_3 and for Fe_3O_4 and FeO above 800 °C the reduction reaction is thermodynamically possible through the solid phase, it is difficult to explain the high rate of iron oxides' reduction under conditions of practically no diffusion of reagents in the solid phase using the provisions of the classical atomic-molecular theory of reduction.

Under these conditions, there are only two ways to accelerate the reduction of iron oxides with carbon:

- (1) In the absence of diffusion of reagents, increase the area and number of their contacts and
- (2) Create conditions for favorable diffusion of reagents.

Table 3. The Content of Iron Oxides in the Slag at Elevated Temperatures.

Temperature, °C	Scale Oxide Content, Mass. %		
	FeO	Fe ₃ O ₄	Fe ₂ O ₃
600	50	50	0
700	98	2	0
800	96	2	2
900	90	9	1
1000	95	4	1

According to [6,19], the area and number of contacts of reacting solid phases can be increased by grinding and subsequent pressing of the mixture components. In [20], the same approach was used in the example of the synthesis of nickel ferrite, zinc aluminates, and magnesium aluminates from oxides under pressure from atmospheric to 60 kbar. The observed strong acceleration of these reactions is explained by an increase in the contact area of the reacting particles and, thus, an improvement in the conditions for diffusion along the interphase surfaces.

The diffusion rate of reactants can be increased by partial destruction of their crystal lattice. This is possible due to the fluxes' introduction into the mixture of scale and carbon, which reduce the melting point of the scale, leading to the formation of local liquid-phase zones, in which the diffusion rate of reacting substances increases by several orders.

2. Materials and Methods

The rolling scale was used in this work as the main studied material. According to the phase analysis results, the scale contained mass.% 43.4 FeO, 27.0 Fe₃O₄, and 29.6 Fe₂O₃, with a Fe_{total} content of 73.4. The coke was used as a reducing agent with a carbon content of 92 mass.%. Its amount was 15% over the stoichiometric ratio. To assess the iron oxides' reduction rate, in the absence of reactants' diffusion, the raw mixture was prepared only from scale and coke. To assess the iron oxides' reduction rate, under conditions of comprehensive diffusion of reacting substances, a flux based on CaO, MgO, SiO₂, Al₂O₃, Na₂O, and CaF₂ was added to the scale and coke mix in an amount of 10 mass.% of the scale [21]. Scale, coke, and flux were dried to a constant mass and joint grinded to a specific surface area by Blain \approx 400 m²/kg. The material mixture of scale, reducing agent, and flux prepared in this way was pressed at pressures of 0, 100, 200, and 300 MPa.

Heat treatment of the pressed raw material mixture was carried out in an argon atmosphere with the removal of gas reaction products. Heating was performed to a temperature of 1200 °C. The thermal characteristics of the raw material mixture were determined during the heating process, and the phase composition of the final products was determined. The crystal phases' identification and their quantitative ratios in the products were determined using X-ray phase analysis. The survey was carried out on an XRD-7000 diffractometer (Shimadzu), in CuK α -radiation (40 kV, 30 mA), graphite monochromator, in the range of scattering angles $2\Theta = 10\text{--}70$ degree, with a step of 0.02 degree. The results were analyzed using the PDF-2 database (Release 2008 RDB 2.0804). Thermal analysis (TA) was performed using the DSC method (differential scanning calorimetry) on the STA 449 F3 Jupiter thermal analyzer (Netzsch-Geratebau GmbH). The experiment was conducted in an argon atmosphere Ar (high purity 99.998%, the volume fraction CO₂ not more than 0.00002%), the gas flow was 30 mL/min, under the condition of linear heating at a speed of 10 °/min, and the temperature measurement error was no more than ± 1.5 degree. Al₂O₃ crucibles with lids were used for the study. Lids were holed to improve the reaction gas exchange. The value of the endothermic effect was calculated in the software module of the device in J/g and converted to kJ/mol by multiplying the data of the device by the mole mass of metallic iron.

3. Results

The pressing pressure influence on the reduction processes of iron oxides of technogenic origin was studied in the absence of a liquid phase (difficult ion diffusion) and with liquid phase if we used flux [21] (developed ion diffusion).

Figure 1 shows the DSC data of the material mixture without the flux addition pressed at pressures of 0, 100, 200, and 300 MPa.

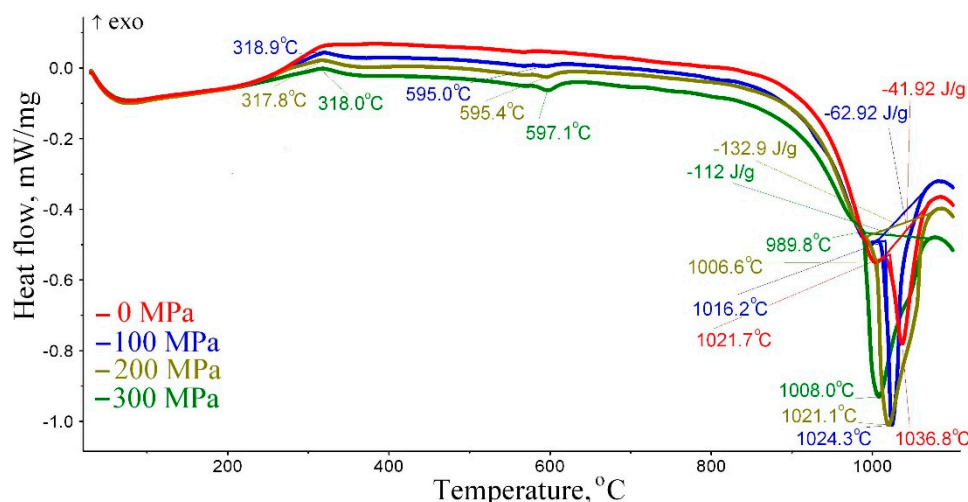


Figure 1. DSC data from of the pressed material mixture of rolled scale and coke without the flux.

Presented data shows that, at the temperature about 300 °C, the processes of heat and mass transfer of reagents reach a value at which the DSC curves are ranked strictly in accordance with the pressure that the scale received during pressing. The DSC of nonpressed scale occupies the upper position and the pressed one at 300 MPa occupies the lower position. The line for not-pressed scale is the upper and the line for scale, pressed at 300 MPa, is the lower. This indicates the pressing limiting influence on the process of studied mixture thermodynamic state converting. Due to a denser contact of the reacting phases, provided by increasing pressing pressure, the thermodynamic state of the mixture changes at the expense of less heat. At a temperature of about 600 °C, a small endothermic effect is observed. It indicates the beginning of the Fe_2O_3 reduction process, according to Reaction (19), which is the first stage of the proposed scale reduction mechanism described below. According to thermodynamic calculations, this reaction is possible starting from the temperature of 539 °C.



Upon further heating at a temperature of about 1000 °C, a small endothermic effect is observed in the nonpressed and pressed scale at 100 MPa, indicating the end of the reducing process of Fe_2O_3 to Fe_3O_4 by Reaction (20) and reducing of Fe_3O_4 to FeO by Reaction (21):



Reactions (20) and (21) are the second stage of the proposed scale reduction mechanism.

DSC data also indicate that, with increasing pressing pressure, the enthalpy of formation of metallic iron and the rate of the reduction reaction increase. The change in these parameters depending on the pressing pressure is given in Table 4.

Table 4. Change in the Metallic Iron Formation Beginning Temperature, the Value of the Endothermic Effect, and the Degree of Metallization of the First Series.

Pressing Pressure, MPa	Temperature of the Metallic Iron Formation Beginning, °C	Enthalpy of Metallic Iron Formation, kJ/mol	Metallization, %
0	1021.7	2.3	34.6
100	1016.2	3.5	49.6
200	1006.6	7.8	66.9
300	989.8	6.6	71.9

In accordance with Table 4, when the pressing pressure increases, the metallization beginning shifts to the lower temperature range from 1021.7 °C at 0 MPa to 989.8 °C at 300 MPa.

As the pressing pressure increases, the enthalpy of metallic iron formation and the degree of metallization also increase. The enthalpy of iron metal formation increases from 2.3 kJ/mol at 0 MPa to 6.6 kJ at 300 MPa. The metallization degree increases from 34.0% to 72%, respectively.

The data of comparative qualitative phase analysis of the pressed mixture without flux, heated in an argon atmosphere, are shown in Figure 2.

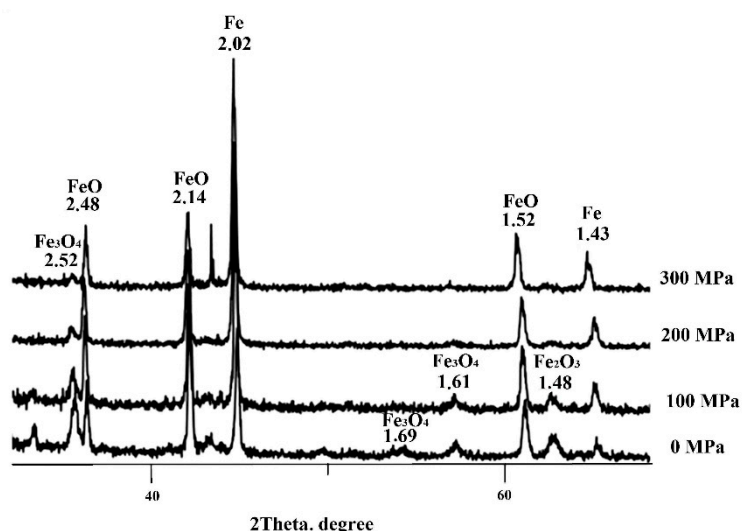
**Figure 2.** Influence of the pressing pressure of a raw mixture without flux heated in an argon medium on the change in its phase composition.

Table 5 shows the phase composition of the firing products according to quantitative phase analysis, depending on the pressing pressure.

Table 5. Firing Products' Phase Composition According to Quantitative Phase Analysis Depending on the Pressing Pressure.

Pressing Pressure of Scale with Coke, MPa	Content, Mass. %			
	Fe ₂ O ₃	Fe ₃ O ₄	FeO	Fe _{met}
0	4.6	19.9	40.9	34.6
100	3.2	14.5	32.7	49.6
200	0	6.5	26.6	66.9
300	0	4.5	23.5	72.0

According to quantitative phase analysis, the residual content of Fe₂O₃ in the heating products of nonpressed scale and pressed at 100 MPa is 4.6% and 3.2%, respectively. There is no Fe₂O₃ in the

heating products of scale pressed at 200 and 300 MPa. Thus, the phase data confirm the conclusions made after DSC analysis, that a small endothermic effect at a temperature of 1000 °C indicates the completion of the reducing process of Fe_2O_3 to Fe_3O_4 . In addition, from the phase analysis data, it follows that under the same conditions of heat treatment, with an increase in the pressing pressure, the content of iron oxide phases decreases from 65.4% for nonpressed scale to 28.0% for scale pressed at 300 MPa. The content of metallic iron, on the contrary, increases.

Figure 3 presents DSC data of pressed mixture with 10% flux.

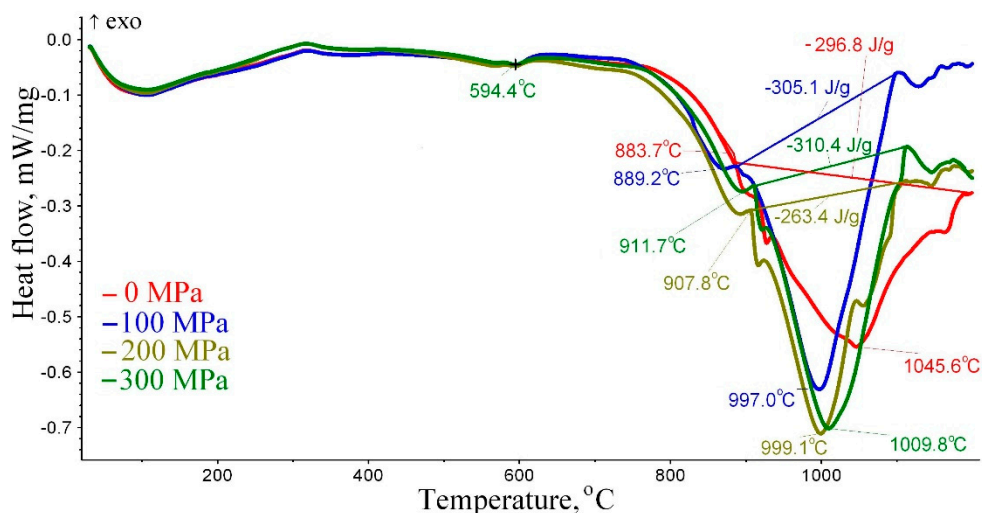


Figure 3. DSC data of the pressed mixture of scale and coke with the addition of 10% flux.

The DSC data presented in Figure 3 show that, at a temperature of 600 °C, all four compositions have a small endothermic effect and the separation of the DSC curves depending on the pressing pressure also begins at this temperature. Small endothermic effects at a temperature of 1000 °C are observed in all compositions.

The change in the temperature of the metallic iron formation beginning and the third series endothermic effect value are shown in Table 6.

Table 6. Change in the Metallic Iron Formation Beginning Temperature, the Value of the Endothermic Effect, and the Degree of Metallization of the Third Series.

Pressing Pressure, MPa.	Temperature of the Metallic Iron Formation Beginning, °C	Enthalpy of Metallic Iron Formation, kJ/mol	Metallization, %
0	883.7	16.6	69.3
100	889.2	17.0	73.6
200	907.8	14.7	64.3
300	911.7	17.4	58.2

According to the Table 6, it can be seen that in the mixture containing flux, with increasing pressing pressure, the temperature of the metallic iron formation beginning rises from 883.7 °C to 911.7 °C, the metal iron formation enthalpy increases slightly from 16.6 kJ/mol at 0 MPa to 17.4 kJ/mol at 300 MPa, and the metallization degree even slightly decreases, respectively, from 69.3% to 58.2%.

The data of comparative qualitative phase analysis of the pressed material mixture with 10% flux, during heating in an argon atmosphere, are shown in Figure 4.

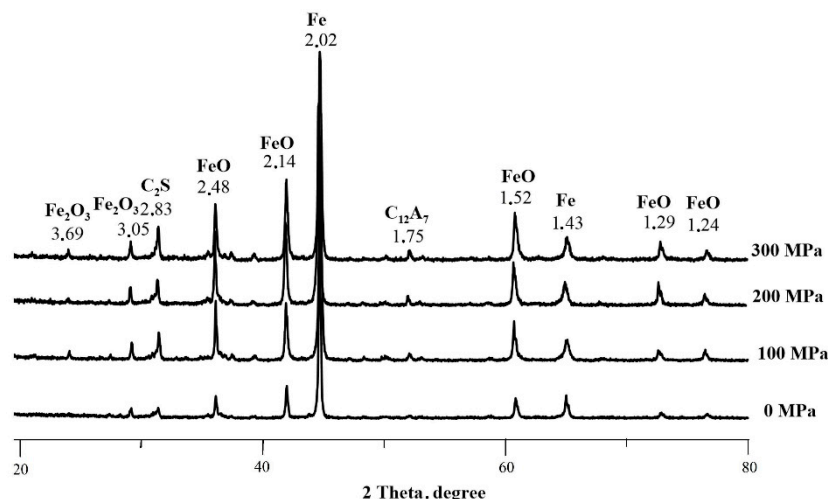


Figure 4. Pressing pressure of the materials' mixture containing flux effect on its phase composition change, during heating in an argon atmosphere.

Table 7 shows the phase composition of firing products with flux according to quantitative phase analysis depending on the pressing pressure.

Table 7. The Phase Composition of Firing Products with Flux According to Quantitative Phase Analysis Depending on the Pressing Pressure.

Pressing Pressure of Scale with Coke and 5% Flux, MPa	Content, Mass. %			
	Fe ₂ O ₃	Fe ₃ O ₄	FeO	Fe _{met}
0	1.9	2.2	31.8	61.9
100	1.8	2.5	26.9	66.4
200	3.1	1.7	34.0	53.2
300	2.5	0	41.4	46.9

The phase analysis data show a small content of hematite and magnetite in the heating products of the mixture containing flux, and it practically does not change with increasing pressing pressure. The FeO content increases with increasing pressing pressure from 31.8% for nonpressed to 41.4% for pressed at 300 MPa scale, and the content of metallic iron, on the contrary, decreases from 69.3% to 46.9%, respectively.

According to the data presented in Figure 4 and Table 7, it can be seen that the pressing pressure does not significantly affect the measured parameters when the material mixture contains 10% of flux, in contrast to the material mixture that does not contain flux.

4. Discussion

The results of thermodynamic analysis show that the recovery of hematite, magnetite, and wustite above the temperature of 700 °C is possible through solid-phase interaction of reagents. Roasting of the mixture based on coke and scale in an argon atmosphere with the gaseous products' removal from the reaction zone, i.e., in conditions that exclude the participation of gaseous products in the recovery process, showed that the recovery processes are successfully implemented with a high degree of metallization through the solid phase.

To explain the observed effects, we propose an ion diffusion-catalytic mechanism of iron oxides' solid-phase reduction, detailing the provisions of the theory of V.E. Roshchin with colleagues [22–26] on the role of electronic processes in the iron oxides' reduction, adapted by us in relation to iron oxides of technogenic origin.

According to this mechanism, at the first stage, the solid-phase interaction of the hematite located on the surface of the scale with the solid carbon located in the intergranular space occurs, with the formation of a CO by Reaction (19). As indicated above, this reaction is possible starting from the temperature of 539 °C. The endothermic effect observed on the DSC curves at a temperature of ≈ 600 °C corresponds to the beginning of the recovery first stage. In accordance with the statements of Roshchin's theory, the metallic iron crystal lattice is a crystal structure with cations at its nodes, and collectivized electrons fill the space between the cations and bind them to the backbone of the crystal lattice. When metal iron is oxidized, oxygen dissolves in it and adds its electronic shell with electrons, becoming an anion. The metal is transformed into a higher oxide after all collectivized electrons become bonded with anions. During reducing, reverse processes occur. Oxygen does not carry away the previously captured valence electrons when extracted from the scale surface due to intergrain carbon interaction, since this would disrupt the charges' balance in the oxide. In our opinion, it transfers electrons to neighboring iron cations. As a result, an oxygen vacuum is formed on the scale surface, two atoms of divalent iron and, respectively, two ionic crystals of wustite.

Resulting wustite are thermodynamically unstable, since they are thermodynamically predisposed to interact with the below hematite layers to form two magnetite molecules by the Reaction (20), which is the beginning of the recovery second stage. At 600 °C, the Gibbs free energy of this reaction is -58.4 kJ/mol. The end of the recovery second stage is the interaction of oxygen of newly formed magnetite molecules with solid intergranular carbon, with the formation of six FeO and CO molecules by Reaction (21). Small endothermic effects of ≈ 1000 °C correspond to the curves of this reaction, and they are observed only in mixtures with a sufficient amount of residual Fe_2O_3 . The Reaction (21) is thermodynamically possible starting from a temperature of 700 °C. As a result of this reaction, oxygen will transfer electrons to neighboring iron atoms with the formation of six divalent iron atoms and the formation of two oxygen vacancies. The newly formed wustite molecules also will be associated with the remaining neighboring hematite molecules with the formation of magnetite molecules. Due to the formation of a wustite molecule's significant number, the catalytic acceleration of the scale reduction processes will occur with the promotion of divalent iron ions deep into the scale and oxygen anions to the surface, in the direction of oxygen vacancies. Due to the catalytic acceleration, provided by the wustite significant amount formation, at the third stage of reducing process, it is restored to metallic iron. At the final stage, only wustite molecules and oxygen vacancies will be located on the scale surface. The wustite oxygen interaction with solid carbon will lead to the metallic iron and CO formation by Reaction (12). According to thermodynamic calculations (Table 1), this reaction is possible from the temperature of 800 °C, and a large endothermic effect in the phase of the highest reaction speed corresponds to this reaction on all DSC curves. During the third stage, oxygen anions will move to the surface and the cations of metallic iron formed during this process will form an apparent flow of movement into the crystal.

The test results show that without the introduction of flux into the material mixture, the pressing pressure has a significant effect on the firing products' phase composition and the recovery process parameters. When the material mixture contains 10% flux, the pressing pressure effect on the firing products' phase composition and the recovery process parameters is minimal. These data indicate that when a sufficient amount of flux is introduced into mixture, the diffusion processes begin to prevail over the dense packing processes associated with pressing pressure. In other words, a sufficient mass of introduced flux eliminates a significant part of process diffusion difficulties, ensuring that the metallization beginning temperature is close to the minimum limit (due to thermodynamics). Also, we can say that the introduction of flux and pressing to some extent have an equivalent effect associated with an increase in the mobility of ions and the growth of the grains' active surface.

5. Conclusions

- (1) Calculations of thermodynamic characteristics and experimental data on the interaction of scale and carbon oxides show the possibility of reducing iron from Fe_2O_3 oxide starting from a

temperature of 700 °C and from Fe₃O₄ and FeO starting from a temperature of 800 °C without the participation of the gaseous phase. The reduction of iron from Fe₃O₄ and FeO oxides with the participation of the gas phase is thermodynamically impossible if the temperature is above 600 °C.

- (2) It was found that, in the absence of a liquid silicate phase, the pressing pressure has a significant effect on the iron oxides' reduction. An increase in the pressing pressure increases the metallization degree and shifts the metallization beginning to the lower temperatures.
- (3) The flux introduction into the system leads to the formation of a liquid silicate phase (at the iron oxides' reduction temperatures). It changes the reduction mechanism. The liquid phase facilitates the processes of diffusion reduction of iron oxides. The pressing pressure in this connection almost has no effect on the temperature of recovery beginning and the metallization degree.
- (4) It is shown that the flux mass (10 mass.%) is sufficient to eliminate a significant part of the diffusion difficulties of the reduction process mechanism and it provides a thermodynamically optimal temperature for the beginning of metallization process.
- (5) The ion diffusion-catalytic mechanism for scale iron oxides' solid-phase reduction is proposed. It details and clarifies the theory of V.E. Roshchin and colleagues in relation to iron oxides of technogenic origin.
- (6) The proposed mechanism basis is the ions' diffusion in conditions of solid-phase reactions, and the catalytic acceleration of that reactions is provided by the avalanche-like appearance of a significant wustite amount.

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